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INFERRING A RELIABLE MECHANICAL STRESS RELAXATION SPECTRUM VIA A REGULARIZATION-QUADRATIC PROGRAMMING TECHNIQUE

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
300 COLLEGE PARK AVENUE
DAYTON, OHIO 45469

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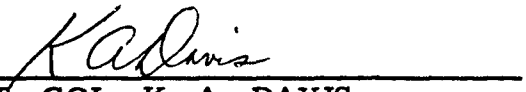

LT. COL. K. A. DAVIS
Project Monitor

FOR THE COMMANDER

DR. R. L. VAN DEUSEN,
Chief, Polymer Branch
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A reliable technique to aid in the prediction of bulk polymer long term mechanical properties is discussed. This technique - regularization and quadratic programming - is applied to the standard NBS isobutylene Master Curve data of Tobolsky and Catsiff. The results show excellent agreement between the mechanical relaxation spectra achieved when no a priori functional form and the published wedge-box functional form are assumed.

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FOREWORD

This report was prepared by the University of Dayton Research Institute, Dayton, Ohio under Contract AF33615-75-C-5095, Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, "New Organic and Inorganic Polymers", with Dr. I. Goldfarb (AFML/MBP) as project engineer.

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The research described in this report was performed at the Polymer Branch Laboratory, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio by Dr. D. R. Wiff of the University of Dayton Research Institute. The manuscript was released by the authors in September 1976 for publication as a technical report.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

INTRODUCTION

Bulk polymeric materials are especially useful in aerospace applications because of their high strength to weight ratio. An example of this from the fiber industry is DuPont's Kevlar. In order to "tailor" bulk polymeric materials for specific applications, through processing or initial synthesis, knowledge of the inherent characteristics of the material is required. Examining each individual material's morphology and correlating this with its mechanical properties is an approach to ultimately "tailor" these materials. If a reliable (straightforward) technique existed for determining the distribution of relaxation times associated with a given mechanical model, a direct one-to-one correlation should exist between this distribution and the material's morphology. In addition, the predictability of long term mechanical properties would be available. It is the purpose of this investigation to present in an illustrative fashion such a technique capable of yielding a reliable distribution of mechanical relaxation times.

BACKGROUND

The problem of inferring mechanical relaxation spectra in linear viscoelastic theory is herein treated as a mathematically ill-posed problem. In previous investigations the established regularization technique of Tikhonov (Reference 1,2) was applied to the mathematically ill-posed problem of inferring a reliable molecular weight distribution from ultracentrifuge sedimentation equilibrium data at a single angular velocity (References 3-5). This technique was further applied (Reference 6) to computer generated data using the well known Fredholm integrals of the first kind encountered in linear viscoelastic theory, namely

$$E_r(t) = \int_{-\infty}^{\infty} H(\tau)\, e(-t/\tau)\, d\ln\tau \tag{1}$$

$$E'(w) = \int_{-\infty}^{\infty} H(\tau) \frac{w^2\tau^2}{1+w^2\tau^2}\, d\ln\tau \tag{2}$$

and

$$E''(w) = \int_{-\infty}^{\infty} H(\tau) \frac{w\tau}{1+w^2\tau^2}\, d\ln\tau \tag{3}$$

where $E_r(t)$ is a stress relaxation modulus, $E'(w)$ and $E''(w)$ are the in-phase and out-of-phase components of the complex dynamic modulus, respectively, and $H(\tau)$ is the sought after relaxation spectra.

The difficulty often mentioned in finding the inverse solution to equations (1), (2) or (3) is experimental error in determining $E_r(t)$, $E'(w)$ or $E''(w)$ can make the determination of $H(\tau)$ futile. As a result iterative approximations have been devised so as to control and limit the occurrence of "wild oscillations" (References 6-12).

The present technique has been successfully applied to computer generated analogous experimental data (Reference 6). Therefore, it was felt that application to real experimental data was now necessary. The data

chosen is the stress-relaxation Master Curve data of NBS polyisobutylene by Tobolsky and Catsiff (Reference 13). In the following, a brief review of the theory of regularization is presented. An attempt is made to convey this theory in light of the method of undetermined multipliers.

THEORY

Rewrite the specific equations (1-3) in a more general form

$$Q[x, f(y)] = \psi(x) = \int_a^b K(x, y)\, f(y)\, dy \qquad (4)$$

where $\psi(x)$ is the experimentally determined function, $f(y)$ is the spectral response function and $K(x, y)$ is the kernel of the appropriate integral equation.

Assume the distribution $f(y)$ is continuous and bounded. Therefore, let $a \leq y \leq b$ and similarly $c \leq x \leq d$. This simply establishes upper and lower limits on the observed relaxation times and frequencies of measurement, respectively. Furthermore, the functions $\psi(x)$ belong to some complete metric space Ψ and the functions $f(y)$ to another complete metric space F, i.e., $\psi \in \Psi$ and $f \in F$. Measuring values of $\psi(x)$ experimentally and knowing the functional form of the integral operator which formally maps $f(y)$ into $\psi(x)$, the inverse solution, i.e., inferring $f(y)$ given $\psi(x)$, is said to be a well posed problem if: (a) the solution exists for $f \in F$, (b) the solution is unique in F, and (c) the solution depends continuously on the metrics of F and Ψ. Tikhonov uses a slightly different concept of correctness. In addition to the spaces Ψ and F and the integral operator, he assumes a closed set $\Lambda \subset F$, $f \in \Lambda$ and all $\psi \in \Lambda'$. Λ' is the image of Λ after application to the space F of the integral operator, i.e., the kernel and integration process (Reference 14). Instead of minimizing the conventional functional

$$N[f(y);\psi(x)] = \int_c^d \{Q[x, f(y)] - \psi(x)\}^2\, dx \qquad (5)$$

Tikhonov suggests minimizing

$$M_n^{\alpha}[f(y);\psi(x)] = N[f(y);\psi(x)] + \alpha\Omega^{(n)}[f(y)] \qquad (6)$$

where $\Omega^{(n)}$ is the regularizing functional, by varying α and choosing that f(y) in correspondence with the $\inf \left|\left|M_n^{\alpha}\right|\right|_{\alpha=o}$. In the present application

$$\alpha\Omega^{(n)}[f] = \sum_{i=o}^{n} \alpha_i \int_a^b [f^{(i)}(y)]^2 \, dy \tag{7}$$

where $f^{(i)}(y)$ is the ith derivative of f(y) with respect to y. Now each α_i is successively varied holding all others constant. In the present application one α_i was sufficient.

From the method of undetermined multipliers presented in elementary calculus (Reference 15), a physical picture of the regularization used in this investigation can be achieved.

Most scientists are familiar with the procedure for obtaining the maxima and minima of a function on the assumption that the variables in the function are linearly independent. However, when the variables are connected by certain relationships, i.e., the variables are not all linearly independent, the maxima and minima are conditional extrema. Consider the function

$$g(x_1, x_2, \ldots x_m, x_{m+1}, \ldots x_{m+n}) \tag{8}$$

of (m+n) variables x_i connected by n relationships

$$\phi_i(x_1, x_2, \ldots, x_m, x_{m+1}, \ldots, x_{m+n}) = 0 \quad (i=1,2,\ldots,n) \tag{9}$$

Let the function g attain a conditional extrema at the point $Q(x_1, x_2, \ldots, x_{m+n})$. Assuming the existence of the derivatives at the point Q, the total differential of g must vanish at Q,

$$\sum_{s=1}^{m+n} \frac{\partial g}{\partial x_s} dx_s = 0 \tag{10}$$

At the same point Q, the following n equations hold [differentiate relationships (9)]

$$\sum_{s=1}^{m+n} \frac{\partial \phi_i}{\partial x_s} dx_s = 0 \quad (i=1,2,\ldots,n) \tag{11}$$

Multiplying these n boundary functions by the factors $\lambda_1, \lambda_2 \ldots, \lambda_n$ (Lagrange multipliers), and adding term by term to equation (10), one obtains

$$\sum_{s=1}^{m+n} \left(\frac{\partial f}{\partial x_s} + \lambda_1 \frac{\partial \phi_1}{\partial x_s} + \lambda_2 \frac{\partial \phi_2}{\partial x_s} + \ldots + \lambda_n \frac{\partial \phi_n}{\partial x_s} \right) = 0 \tag{12}$$

Usually these n factors are defined such that the n differentials of the dependent variables vanish.

It seems reasonable to assume that the present integral equations under consideration [equations (1)-(3) or equation (4)] could have variables which are not linearly independent, especially when "large" errors exist in the experimentally determined functions, i.e. $\{\psi(x)\}$. These errors might not seem large, but if the inverse transformation needed to infer $\{f(y)\}$ acts as an "amplifier" of noise. Then minimizing $N[f(y);\psi(x)]$ i.e., eqn. (5) will not yield absolute extrema but rather conditional extrema. Not knowing exactly the constraints required to control this "noise" one would be led to apply the logic implied by equation (12). That is, assume various derivatives of f(y) are the constraints and vary the λ's (in our nomenclature α_i) until a minimum in the error analysis is achieved. The "best fit" solution $f^*(y)$ will then be that in correspondence with the smallest or inferior of all the individual conditional minima. It is just this technique which has been applied using equations (6) and (7) along with the computational scheme of quadratic programming (Reference 16). The unique advantage attained in use of the quadratic programming algorithm is that only positive values for f(y) are admissible. Recall f(y) is the sought after spectral response function and negative values would not have physical meaning.

RESULTS

The present technique using regularization and quadratic programming was applied to the experimental stress relaxation, Master Curve, data published by Tobolsky and Catsiff (Reference 13). The values of $\log E_r(t)$ are presented in Table 1 along with the corresponding logarithm of the observation times. It should be noted that even though the data appear to be smooth on a logarithmic scale, on an absolute scale values may have large fluctuations. That is, if

$$[\log E_r(t_i)]_{exp} = [\log E_r(t_i)]_{True} + \delta \tag{13}$$

$$\text{where } \delta = \log \epsilon$$

then

$$E_r(t_i)\big|_{exp} = \epsilon\, E_r(t_i)\big|_{True} = 10^{\delta} E_r(t_i)\big|_{True} \tag{14}$$

Computationally we deal with actual values in equation (4). These fluctuations in the experimental data have a profound influence on the inverse operational matrix, which is required for inferring f(y). The results of the present computation are numerically given in Table 1. The relaxation spectrum was not computed at the same relaxation times as those listed in the first column. Therefore, the inferred $\log H(\tau)$ and $\log \tau$ values are presented in the last two columns. They are spread out in the display for ease of comparison between $\log H(\tau)$ and $\log H(\tau')$. The results are graphically displayed in Figures 1 and 2. In Figure 1 the inferred distribution is represented by circles and the 'best fit" parameterized "wedge and box" distribution of Tobolsky and Catsiff is the solid line. Using the circled data of Figure 1 or the data in the last two columns of Table 1 and equation (3), the computed stress relaxation values, column four of Table 1 and circled points in Figure 2, were determined. To achieve these results, each

individual $f^{(i)}(y)$ [equation (7)] was independently applied. The corresponding α_i was varied and the distribution in correspondence with the minimum of coefficient of variation between the experimental $E_{r,298}(t)$ and the calculated $E_r(t)$ was used. The chosen distribution was in correspondence with the inferior of these minima coefficients of variation. In the present case for i=1,

$$\alpha_1 \int_a^b \left(\frac{df(y)}{dy} \right)^2 dy \tag{15}$$

was the regularization function yielding $\inf ||E_r(t)_{exp} - E_r(t)_{calc}||$.

CONCLUSION

A computational technique is of value to an experimenter if it is reliable, easy to use, and does not consume a large amount of high speed digital computer time. In the present case, the reproducibility of the log $H(\tau)$ distribution almost identical to that achieved by the "a priori" functional "wedge-box" shape is very encouraging. The only restriction on the sought after distribution, in the present case, is that the boundaries of the range of relaxation times be broad enough so that the function and its derivatives vanish at the boundaries and that the function is continuous. The present technique is easy to use because of the simplicity of the mathematical concepts. Finally, the computational time required for a broad search of numerical values e.g., $10^{-20} \leq \alpha \leq 10^{20}$ required only about one second central processing time on a CDC CYBER 70 computer. With experience an investigator should know which α_i to search and depending upon his usual experimental error, the approximate range of numerical values to scan. This will further reduce the actual computational time.

Having the capability to easily infer a relaxation spectra from experimental mechanical data within the regime of linear viscoelasticity, one is led to apply the technique to data from a variety of specimens. As mentioned within the text this will allow a correlation between mechanical model relaxation spectra $H(\tau)$ and the observed morphology. This should be a step toward eventual "tailoring" molecular level processes to yield desired macroscopic end use morphologies. It is realized that this is a long term process. However, another more immediate use of this new capability will be the time saving in being able to do a few experiments and, using existing viscoelastic theories, predict other unmeasured mechanical behavior of the material. This will especially be of value for long time mechanical behavior. Again one should remember that the predictions are only as good as the theories used in the extrapolation of information. That is, there will always be the need for experimental checking, but the number of experiments performed will decrease as confidence in the theory increases.

Finally, since the present investigation concerns itself only with linear viscoelastic theory, the greatest impact will come by extending these ideas to the nonlinear viscoelastic regime.

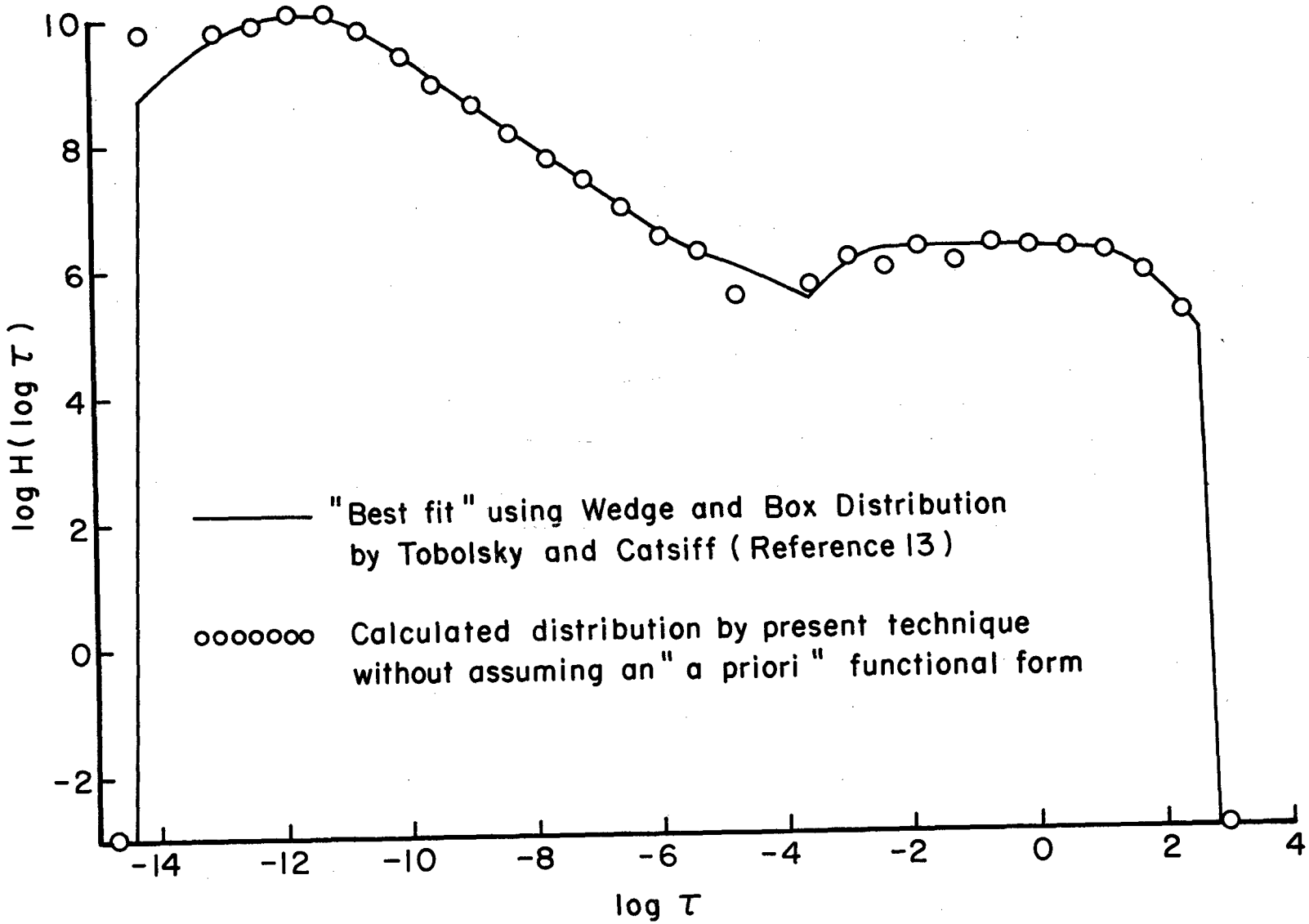

Figure 1. A Comparison of the Relaxation Spectra Obtained by the Present Technique and by Assuming an Initial Functional Form.

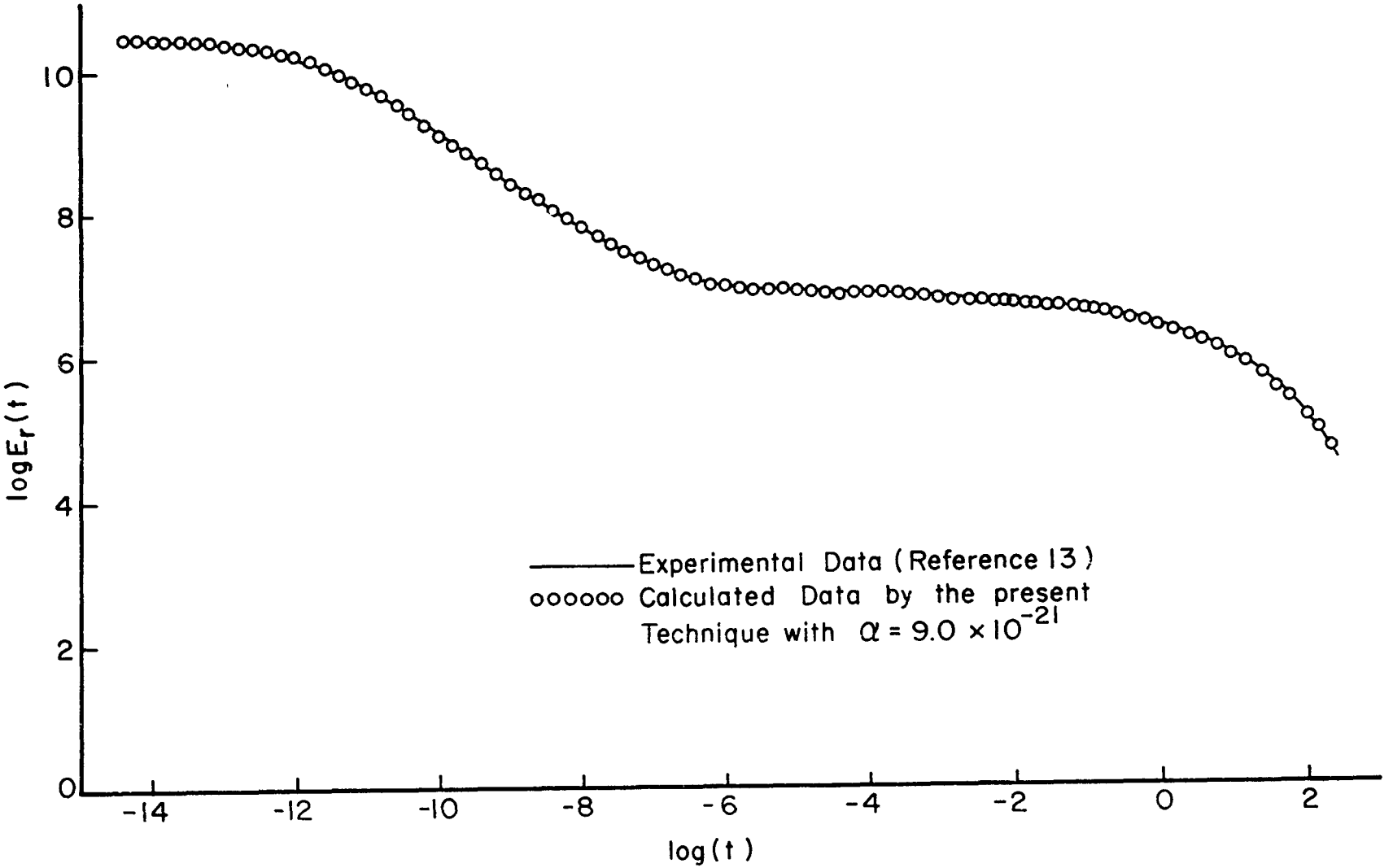

Figure 2. The Stress Relaxation Curves in Correspondence with the Two Relaxation Spectra Presented in Figure 1.

TABLE 1

Comparison of Mechanical Relaxation Spectrum When "a priori" Wedge-Box Shape is Assumed[a] and When No Previous Functional Form is Assumed (Regularization Technique Applied)

(The stress-relaxation data (dyne/cm^2) calculated is also presented)

log t log τ (hr)	Tobolsky & Catsiff[a]		Regularization Technique		
	log $E_{r,298}(t)$	log H (log τ)	log $E_r(t)_{calc}$	log H (log τ')	log τ' hr
-14.4	10.48		10.52		
.2	10.48	8.77	10.50	9.81	-14.2
.0	10.46	8.96	10.49		
-13.8	10.45	9.12	10.47		
.6	10.44	9.27	10.46		
.4	10.43	9.41	10.45		
.2	10.41	9.55	10.43		
.0	10.39	9.66	10.41	9.82	-13.0
-12.8	10.37	9.77	10.38		
.6	10.34	9.84	10.35		
.4	10.30	9.91	10.31	9.87	-12.4
.2	10.25	9.96	10.27		
.0	10.20	10.01	10.21		
-11.8	10.15	10.03	10.15	10.10	-11.8
.6	10.07	10.05	10.07		
.4	9.98	10.04	10.01		
.2	9.88	9.99	9.89	10.11	-11.2
.0	9.77	9.93	9.79		
-10.8	9.65	9.87	9.68		
.6	9.52	9.76	9.55	9.81	-10.7
.4	9.39	9.64	9.40		
.2	9.26	9.50	9.24	9.41	-10.1
.0	9.12	9.35	9.11		
-9.8	8.99	9.21	8.99		
.6	8.86	9.09	8.87	8.98	-9.5
.4	8.73	8.95	8.76		
.2	8.60	8.83	8.59		
.0	8.47	8.70	8.45	8.69	-8.9
-8.8	8.33	8.57	8.32		
.6	8.19	8.43	8.19		
.4	8.05	8.27	8.01		
.2	7.92	8.11	7.94	8.15	-8.3
.0	7.80	7.96	7.81		

TABLE 1 (Continued)

log t log τ (hr)	Tobolsky & Catsiff[a]		Regularization Technique		
	log $E_{r,298}(t)$	log H (log τ)	log $E_r(t)_{calc}$	log H (log τ')	log τ' hr
-7.8	7.69	7.83	7.70		
.6	7.58	7.71	7.59	7.80	-7.7
.4	7.48	7.58	7.50		
.2	7.38	7.46	7.41	7.44	-7.1
.0	7.29	7.33	7.31		
-6.8	7.21	7.20	7.24		
.6	7.14	7.05	7.13	6.96	-6.5
.4	7.08	6.88	7.07		
.2	7.04	6.72	7.03		
.0	7.00	6.60	6.98		
-5.8	6.98	6.48	6.97	6.45	-5.9
.6	6.96	6.35	6.95		
.4	6.94	6.26	6.93	6.37	-5.3
.2	6.92	6.16	6.92		
.0	6.91	6.07	6.91		
-4.8	6.90	5.97	6.90	5.55	-4.7
.6	6.90	5.87	6.90		
.4	6.89	5.78	6.89		
.2	6.89	5.68	6.89		
.0	6.88	5.58	6.89		
-3.8	6.88	5.49	6.88		
.6	6.87	5.41	6.86	5.79	-3.5
.4	6.87	5.45	6.86		
.2	6.85	5.75	6.85		
.0	6.84	5.96	6.84		
-2.8	6.82	6.07	6.82	6.14	-2.9
.6	6.81	6.14	6.81		
.4	6.79	6.18	6.79		
.2	6.78	6.20	6.76	5.90	-2.3
.0	6.75	6.20	6.73		
-1.8	6.73	6.21	6.73	6.29	-1.8
.6	6.71	6.21	6.70		
.4	6.68	6.21	6.68		
.2	6.65	6.21	6.65	6.02	-1.2
.0	6.62	6.22	6.62		

TABLE 1 (Concluded)

log t log τ (hr)	Tobolsky & Catsiff[a]		Regularization Technique		
	log $E_{r,298}(t)$	log H (log τ)	log $E_r(t)_{calc}$	log H (log τ')	log τ' hr
-0.8	6.59	6.22	6.59		
.6	6.55	6.22	6.55	6.32	-0.6
.4	6.50	6.22	6.52		
.2	6.45	6.22	6.46		
.0	6.39	6.22	6.40	6.24	0.0
0.2	6.33	6.22	6.34		
.4	6.26	6.22	6.26		
.6	6.17	6.22	6.18	6.27	0.6
.8	6.08	6.19	6.09		
1.0	5.97	6.14	6.00		
.2	5.85	6.08	5.87	6.13	1.2
.4	5.70	6.00	5.72		
.6	5.54	5.89	5.53		
.8	5.34	5.74	5.33	5.82	1.8
2.0	5.18	5.57	5.14		
.2	4.90	5.38	4.94		
.4	4.50	5.18	4.71	5.18	2.4
.6	4.00	4.98			

[a] See reference 13.

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